

9-Methyl-3-phenyldiazenyl-9*H*-carbazole: X-ray and DFT-calculated structures

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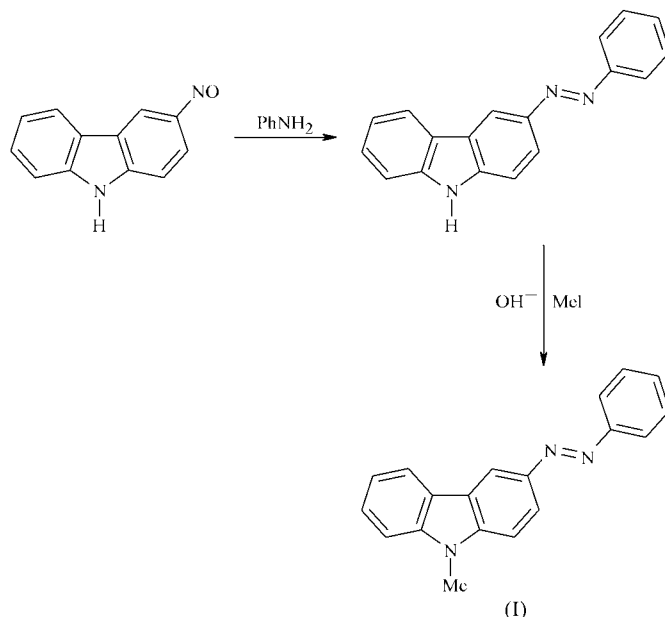
The title compound, $C_{19}H_{15}N_3$, was prepared by condensation of 3-nitrosocarbazole and aniline with subsequent methylation. The structure is built up of stacks of almost planar molecules. Density functional theory (DFT) calculations predict a completely planar conformation, different from that observed in the crystal lattice. HOMA (harmonic oscillator model of aromaticity) indices, calculated for three aromatic rings, demonstrate the small influence of the azo substituent on π electrons in the carbazole system.

Comment

The carbazole system is susceptible to electrophilic attack but not enough to couple with diazonium salts. Carbazol-3-yl-diazonium salts can be generated *in situ* and coupled with very reactive substrates such as 2-naphthol. A more general method of preparation involves condensation of nitrosoarenes and amines. 3-Phenyldiazocarbazole was prepared, in moderate yield, from 3-nitrosocarbazole and aniline in acetic acid solution. Its 9-methyl derivative, (I), formed orange well shaped crystals suitable for X-ray diffraction studies. The reversed sequence of steps, *viz.* methylation and condensation, is less effective due to the side reactions that accompany alkylation of 3-nitrosocarbazole (Kyzioł, 1985).

The intense colour of (I) and its high dipole moment ($\mu = 7.47 \times 10^{-30}$ Cm), suggested conjugation between the azo bridge and carbazole system (Frej *et al.*, 1990). In the UV–vis spectrum (in THF), a strong band near the visible borderline ($\lambda_{\max} = 390$ nm, $\log \epsilon = 3.98$) corresponds to the *K*-band in azobenzene ($\lambda_{\max} = 315$ nm, $\log \epsilon = 4.35$). Such a bathochromic shift reflects enhanced polarizability of the carbazole system in comparison with the benzene ring, and a conjugation between aromatic π electrons and those of the azo bridge. Such an interaction should result in a planar conformation of the molecule of (I); indeed, the mean deviation from the C3/N1/N2/C1B plane does not exceed 0.003 Å and both aromatic rings are nearly coplanar with the azo bridge (Fig. 1). The torsion angle along the C1B–N2 bond is 9.8 (2)° (Table 1),

the other angle about C3–N1 is even smaller [4.4 (2)°] and the aromatic rings are twisted in opposite directions. These small deformations probably result from the intermolecular interactions in the crystal lattice. A density functional



theory (DFT) study predicts a completely planar conformation as the preferential one for the isolated molecule of (I), like that presented in the scheme (the N1–N2 bond *syn* to the C2–C3 bond). Another planar conformation (the N1–N2 bond *anti* to the C2–C3 bond), resulting from the former by rotation of 180° along the C3–N1 bond, is more stable by 0.3 kcal mol⁻¹. However, in the crystal lattice, the latter is actually observed. Rotation along the Ar–N bonds is fast in the NMR time scale. Comparison of the spectra of (I), azobenzene and 9,9'-dimethyl-3,3'-azocarbazole allows for unequivocal assignment of the signals. There are only four peaks coming from the benzene ring since the signals of atoms C2B and C6B and those of C3B and C5B are isochronic. The

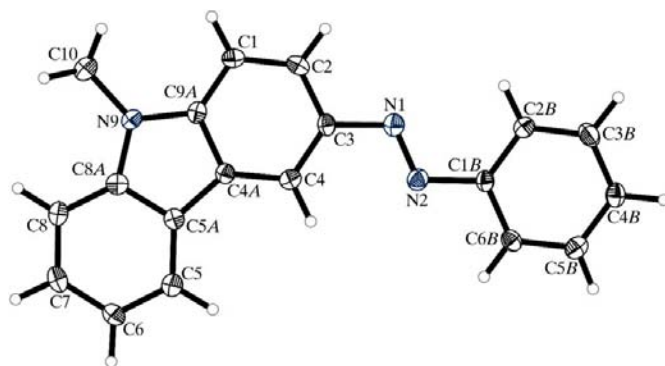


Figure 1
The molecular structure of (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

B3LYP/6-311+G** calculations indicated that the rotational barrier along the N2—C1B bond is *ca* 5 kcal mol⁻¹ and slightly higher (*ca* 8 kcal mol⁻¹) on the other side of the azo bridge. The torsion barrier of a phenyl ring corresponds well to the torsional potential found in *trans*-azobenzene (Tsuji *et al.*, 2001).

The geometry of the azo bridge is typical of azoarenes; however, the N1=N2 bond [1.269 (2) Å] is slightly longer than in other compounds of this type (Allen *et al.*, 1995). In azobenzene and its *para*-substituted derivatives, the N=N distance lies within the range 1.232–1.255 Å, characteristic of the strictly double-bond character (Allmann, 1975). The N1—C3 and N2—C1B bonds [1.432 (2) and 1.426 (2) Å, respectively] are longer than typical single bonds between *sp*²-hybridized N and C atoms (Allen *et al.*, 1995). The valence angles centred on N1 and N2 are less than 120° [113.3 (1) and 114.4 (1)°, respectively] and, consequently, the C3—N1 and C1B—N2 bonds deviate from the symmetry axis of the benzene rings. Enhancement of the C4—C3—N1 and C2B—C1B—N2 valence angles increases the distance between *ortho* H atoms and azo N atoms to the acceptable values. The other geometric parameters of the *N*-methylcarbazole group in (I) correlate well with the corresponding values found in the crystal structure of 9-methylcarbazole (Popova & Chetkina, 1978) and its charge-transfer complexes (Hosomi *et al.*, 2000). There are no significant differences between the values of bond lengths and angles of (I) in the solid state and in the calculated structure; the differences do not exceed 0.02 Å for bond distances and 2° for bond angles.

Deformations of the benzene ring are not observed in spite of the electron-withdrawing properties of the azo group (Domenicano, 1992); the HOMA (harmonic oscillator model

of aromaticity) index (Kruszewski & Krygowski, 1973; Krygowski, 1993) indicates that aromaticity of the ring is not disturbed (HOMA = 0.993). The benzene rings belonging to the carbazole system are not regular hexagons but they do not differ significantly from the rings in 9-isopropylcarbazole (Baert *et al.*, 1986); however, the HOMA indices differ to some extent. The value for the substituted ring (0.937) is lower than that of the other ring (0.961). The same sequences of values were obtained for hypothetical conformations, *viz.* planar and twisted by 90°. Significant quinonoid deformation of the substituted carbazole ring was not observed, despite the delocalization of the electron pair on the pyrrole N atom. Atom N9 lies in the plane defined by the neighbouring C atoms. The N9—C8A and N9—C9A bond lengths [1.394 (2) and 1.385 (2) Å, respectively] correspond to a bond order of 1.2. The electron-withdrawing properties of the phenylazo group ($\sigma_p = +0.39$) are insufficient to disturb the carbazole aromatic system. The conjugation between aromatic π -electrons and those of the azo bridge is not strong enough to cause significant deformations in the molecular structure.

The molecular arrangement of (I) in the crystal state is presented in Fig. 2. The molecules form columns with a parallel arrangement; the distance between stacked molecules, measured as the distance between mean planes of non-H atoms, is 3.386 (1) Å. The molecules are shifted in the column in a staircase manner, so azo atom N2 is 3.375 (1) Å from ring atom C5B. The molecules belonging to the neighbouring columns form a dihedral angle of 78.21 (1)°.

Experimental

For the preparation of 3-(phenylazo)carbazole, 3-nitrosocarbazole (1.96 g, 10 mmol) and freshly distilled aniline (1.01 ml, 11 mmol) were dissolved in a mixture of methanol (50 ml) and acetic acid (50 ml). The brown solution was maintained at 323 K for 4 h and evaporated in a vacuum. A tarry residue was chromatographed on a column (40 × 5 cm, silica gel, type 60) using benzene as the eluant. The orange solution was concentrated to *ca* 100 ml, diluted with an equal volume of isooctane and cooled. 3-(Phenylazo)carbazole (1.35 g, 50%) was collected by filtration and dried in a vacuum (m.p. 473–474 K). Recrystallization from ethanol did not change the melting point. MS, *m/z* (int.): 271 (38, M⁺), 241 (3), 194 (11), 167 (17), 166 (100), 138 (21), 92 (5), 91 (7), 77 (18). IR (KBr): 3405 (pyrrole H atom); 3060 (stretching vibrations of aromatic H atoms); 1610, 1455, 1330, 1250 (skeletal vibrations); 825 (out-of-plane wagging vibrations, two adjacent H atoms); 760, 735 (four adjacent H atoms wagging); 700 (sextant ring bend). ¹³C NMR (CDCl₃, p.p.m.): phenyl ring 153.1 (C1B), 130.4 (C4B), 129.3 (C3B and C5B), 122.8 (C2B and C6B); carbazole system 146.9 (C3), 141.5 (C9A), 140.4 (C8A), 126.7 (C7), 124.1 (C4A), 124.0 (C5A), 121.3 (C2), 121.0 (C5), 120.5 (C6), 117.0 (C4), 111.2 (C1), 111.0 (C8). Analysis calculated for C₁₈H₁₃N₃: C 79.68, H 4.83%; found: C 79.79, H 4.98%. For the preparation of (I), 3-(phenylazo)carbazole (2.71 g, 10 mmol), methyl iodide (2.84 g, 20 mmol) and tetra-*n*-butylammonium iodide (0.1 g) were dissolved in dimethyl sulfoxide (10 ml). To the stirred solution, potassium hydroxide (4.6 g, 0.1 mol), as a concentrated aqueous solution, was added and stirring was continued for 2 h. The mixture was poured on to ice, and a yellow precipitate was collected by filtration and crys-

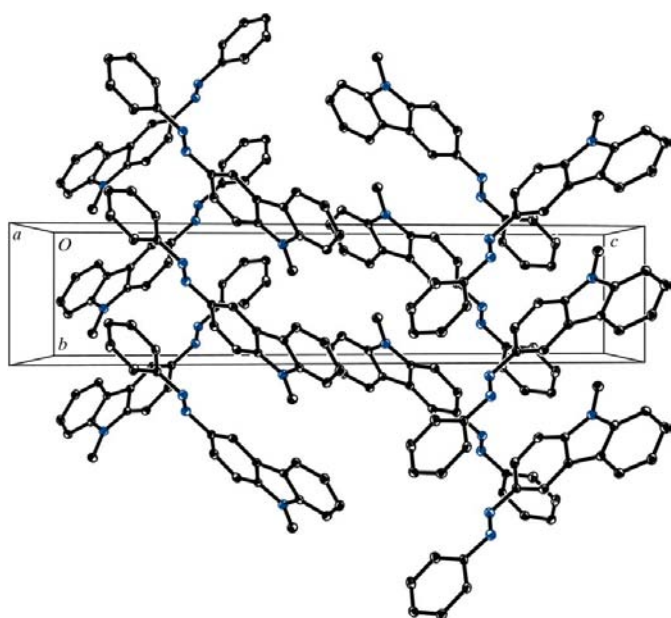


Figure 2
The packing of (I), viewed down *a*.

tallized twice from ethanol. Compound (I) (2.19 g, 80%) was obtained as orange needles (m.p. 405–406 K). MS, m/z (int.): 285 (44, M^+), 208 (3), 180 (100), 164 (4), 152 (24), 77 (12). IR (KBr): 3050 (aromatic H atoms); 2932, 2822 (*N*-methyl group); 1425 (deformations of *N*-methyl group); 745 (deformations of four and five adjacent aromatic H atoms); 686 (mono-substituted benzene ring bend). ^{13}C NMR (CDCl_3 , p.p.m.): phenyl ring 153.1 (C1B), 130.3 (C4B), 129.3 (C3B and C5B), 122.7 (C2 and C6B); carbazole system 146.4 (C3), 142.9 (C9A), 141.9 (C8A), 126.5 (C7), 123.6 (C4A), 123.3 (C5A), 121.3 (C2), 120.9 (C5), 120 (C6), 116.8 (C4), 109.2 (C1), 108.8 (C8). The crystal-state geometry of (I) was used as the starting structure for full optimization using standard DFT and employing the B3LYP hybrid functional (Becke, 1988, 1993; Lee *et al.*, 1988). Geometry optimization and vibrational analysis were performed without constraints on isolated molecules using the 6–311+G** basis set. All normal frequencies at the optimized geometry are real, showing that it is indeed a stable minimum. The calculations were carried out using GAUSSIAN03 (Frisch *et al.*, 2004).

Crystal data

$\text{C}_{19}\text{H}_{15}\text{N}_3$	$Z = 4$
$M_r = 285.34$	$D_x = 1.330 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 10.8631 (9) \text{ \AA}$	$\mu = 0.08 \text{ mm}^{-1}$
$b = 5.3684 (5) \text{ \AA}$	$T = 90.0 (1) \text{ K}$
$c = 24.661 (2) \text{ \AA}$	Cube, orange
$\beta = 97.833 (7)^\circ$	$0.28 \times 0.25 \times 0.22 \text{ mm}$
$V = 1424.7 (2) \text{ \AA}^3$	

Data collection

Xcalibur diffractometer	1400 reflections with $I > 2\sigma(I)$
ω scans	$R_{\text{int}} = 0.048$
10582 measured reflections	$\theta_{\text{max}} = 25.5^\circ$
2656 independent reflections	

Table 1

Comparison of selected geometric data for (I) (\AA , $^\circ$) from X-ray and calculated (DFT) data.

	X-ray	DFT
N1–N2	1.269 (2)	1.255
N1–C3	1.432 (2)	1.412
N2–C1B	1.426 (2)	1.419
N9–C9A	1.385 (2)	1.383
N9–C8A	1.394 (2)	1.393
N9–C10	1.456 (2)	1.449
N2–N1–C3	113.3 (1)	115.83
N1–N2–C1B	114.4 (1)	115.26
C6B–C1B–N2	115.3 (1)	115.83
C2B–C1B–N2	124.6 (2)	124.73
C9A–N9–C8A	109.1 (1)	108.84
C9A–N9–C10	126.0 (1)	125.82
C8A–N9–C10	124.8 (1)	125.22
N9–C8A–C5A	108.9 (1)	109.06
N9–C9A–C4A	108.7 (1)	109.05
C3–N1–N2–C1B	–179.5 (1)	179.98
N1–N2–C1B–C6B	–170.9 (1)	179.80
N1–N2–C1B–C2B	9.8 (2)	–0.20
N2–N1–C3–C4	–4.4 (2)	–0.48
N2–N1–C3–C2	175.2 (1)	179.80

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0778P)^2 + 0.1154P]$
$R[F^2 > 2\sigma(F^2)] = 0.034$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.058$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 0.84$	$\Delta\rho_{\text{max}} = 0.14 \text{ e \AA}^{-3}$
2656 reflections	$\Delta\rho_{\text{min}} = -0.19 \text{ e \AA}^{-3}$
247 parameters	
H atoms treated by a mixture of independent and constrained refinement	

The H atoms of the methyl group were generated in idealized positions, with the torsion angle optimized ($\text{C–H} = 0.96 \text{ \AA}$). The remaining H atoms were localized successfully from a Fourier map and in the final refinement their positions and isotropic displacement parameters were refined; the final C–H distances ranged from 0.951 (13) to 1.034 (14) \AA .

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2002); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2002); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1990); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: HJ3027). Services for accessing these data are described at the back of the journal.

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